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REACTIONS OF TUNGSTEN-DINITROGEN COMPLEXES WITH IODOTRIMETHYLSILANE. FORMATION OF Si-N BOND FROM LIGATING DINITROGEN[1)]

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The dinitrogen complex cis-$[W(N_2)_2(PMe_2Ph)_4]$ reacts with Me_3SiI at 50 °C to give $[WI(N_2SiMe_3)(PMe_2Ph)_4]$, which is further converted into $[WI_2(N_2HSiMe_3)(PMe_2Ph)_3]$ by treatment with HI. The molecular structure of the latter complex has been determined by X-ray crystallographic analysis, which clearly shows the Me_3Si group bonded to the β-nitrogen from the metal.

Extensive studies on the reactivities of ligating dinitrogen have revealed that the terminal nitrogen atom in ligating dinitrogen undergoes electrophilic attack by proton and Lewis acids.[2)] These findings have led us to expect that Me_3SiI might react with ligating dinitrogen since the Me_3Si group behaves as a good electrophile. We wish here to describe the formation of Si-N bond from the reaction of Me_3SiI and tungsten dinitrogen complexes $[W(N_2)_2(L)_4]$ (L = phosphine). These reactions may have some relevance to the reductive silylation of dinitrogen to tri(trialkylsilyl)-amine, which has been achieved by the reaction of N_2, Me_3SiCl and Li in the presence of transition metal complexes such as $CrCl_3$.[3)]

Treatment of the dinitrogen complex cis-$[W(N_2)_2(PMe_2Ph)_4]$ with an excess of Me_3SiI in benzene at 50°C for one day in the dark evolved one mole of dinitrogen per W atom. Addition of hexane to a concentrated dark-red solution gave a trimethylsilyldiazenido complex $[WI(N_2SiMe_3)(PMe_2Ph)_4]$ (I) and a trimethylsilylhydrazido(2-) complex $[WI_2(N_2HSiMe_3)(PMe_2Ph)_3]$ (II) in 42 and 16 % yields, respectively, as a separable mixture of yellow and dark-red crystals. The elemental analysis of (I) is consistent with its formulation as the diazenido complex. The infrared spectrum of (I) shows a strong band at 1570 cm^{-1} assigned to $\nu(N_2)$ and a band at 873 cm^{-1} assigned to ν(Si-N). The analytical data of (II) is also satisfactory. The complex (II) gives rise to a band at 3250 cm^{-1} in the infrared spectrum assigned to ν(N-H) in addition to a strong band at 1355 cm^{-1} associated with $\nu(N_2)$ and a band at 840 cm^{-1} characteristic of ν(Si-N). The ^1H-NMR spectrum of the complex (II) shows two singlet peaks at 2.13 and -0.02 ppm which we assign to the N-H and Si-CH_3 protons, respectively, in addition to resonances characteristic of P-C_6H_5 and P-CH_3 protons, which integrate in the correct intensity ratio.

The complex (II) may be formed by the reaction of the complex (I) with HI, which arises from hydrolysis of Me_3SiI by adventitious water.

$$\text{cis-}[W(N_2)_2(PMe_2Ph)_4] \quad + \quad Me_3SiI \longrightarrow [WI(N_2SiMe_3)(PMe_2Ph)_4] \quad \text{(I)}$$

$$(I) + 2HI \longrightarrow [WI_2(N_2HSiMe_3)(PMe_2Ph)_3]\ (II) + [HPMe_2Ph]I$$

The molecular structure of the complex (II) has been determined by X-ray crystallographic analysis.[4)] A stereoview of the complex is shown in Figure 1, indicating that the W-N-N linkage is essentially linear and the Me_3Si group is bonded to the nitrogen atom at the β-position from the metal. The W-N and N-N bond lengths are 1.77(2) and 1.32(3) Å, respectively, which are very similar to those of a methylhydrazido(2-) complex $[WBr(N_2HMe)(dppe)_2]Br$.[5)] However, the N-N-Si bond angle of 126.6(17)° is rather larger than the N-N-C bond angle of 121° of the methylhydrazido(2-) complex. This may arise from bulkiness of the Me_3Si group.

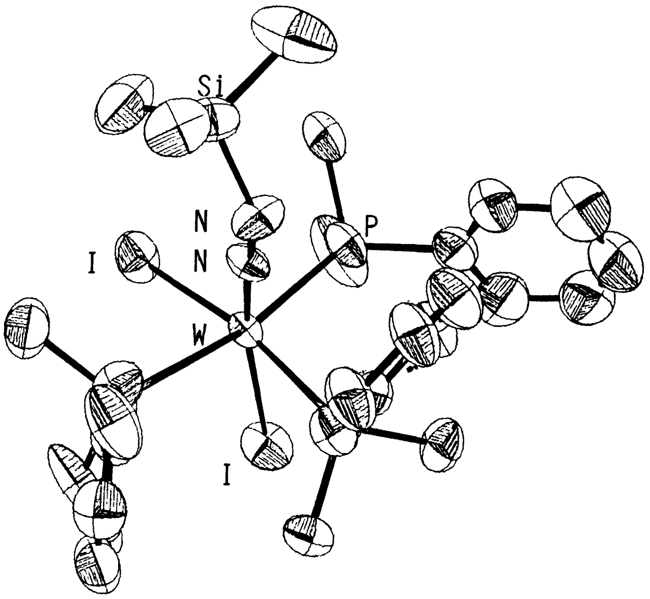

Figure 1. A stereoview of the structure of $[WI_2(N_2HSiMe_3)(PMe_2Ph)_3]$

A similar complex is also obtained from trans-$[W(N_2)_2(dppe)(PMePh_2)_2]$ and Me_3SiI. Investigation on the reactivities of the complexes described above are currently under way.

References

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4) The complex crystallized in the monoclinic space group $P2_1/n$ with cell dimensions a = 17.418(4), b = 18.031(5), c = 11.370(2) Å and β = 91.61(2)°. Diffraction data were collected on a Rigaku automatic four-cycle diffractometer; 6441 reflections ($|Fo| \geqq 3\sigma|Fo|$) were used in the structure solution and refinement. The final residuals were R = 0.13, Rw = 0.15 using block-diagonal least-squares with anisotropic thermal parameters for nonhydrogen atoms.

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